JOURNAL OF OPTOELECTRONICS AND ADVANCED MATERIALS, Vol. 11, No. 2, February 2009, p. 91 - 103

Relationship between optical absorption and photoluminescence in non-crystalline semiconductors

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Employing a barrier-cluster model, we attempt to explain qualitatively some experimental data on photoluminescence in non-crystalline semiconductors. We discuss the dependence of the photoluminescence intensity on the energy of quanta of the primary light irradiation in the exponential tail region of the optical absorption

(Received January 23, 2009; after revision February 14, 2009; accepted February 23, 2009)

Keywords: Chalcogenide glass, Cluster, Barrier-cluster model, Optical absorption, Photoluminescence, Amorphous, Semiconductor, Non-crystalline semiconductor

1. Introduction

1.1 Chalcogenide glasses

The amorphous semiconductors and particularly the chalcogenide glasses attract strong scientific interest due to the advantages from practical point of view [1-4]. They are suitable material for optical elements, optical memory disc, functional elements in integral-optic system, IR-fibres that show high flexibility and chemical durability etc. The great advantages of the disordered materials are: simple preparation procedures, low sensitivity to impurities, low cost, and, last but not least, the possibility to produce large area films of various tickness in classical system for deposition: system for evaporation in vacuum, magnetron systems, flash, spin-coating system, sol-gel system etc.

Up to day it does not exist an universal material, as silicon in microelectronics, which would satisfy all requirements of the photonics. In different laboratories around the world, various materials are studied, intended to cover a large number of technical possibilities. Among the groups of materials under focusing for optoelectronic applications, a special place is occupied by the non-crystalline semiconductors, based on chalcogenides with special properties. A great number of amorphous chalcogenide materials is successfully applied or are of potential interest for optoelectronics.

From practical point of view there are important: wide region of optical transparency of chalcogenide glasess, high refractive index, photoinduced effects, witch are accompanied by considerable changes in the value of the optical constants as a result of the structural changes of these materials.

A considerable attention was devoted to optical phenomena in non-crystalline semiconductors, including absorption and luminescence, in the past decades. Reports on many experimental observations were published.

Although the chalcogenide glasses, a particular class of non-crystalline semiconductors, are widely used in modern technology, many physical processes in these materials are not fully undestood. The non-crystalline semiconductors generate a number of complex problems. There is no generally accepted theory of non-crystalline semiconductors, that could explain all observed phenomena.

The fundamental knowledge of non-crystalline semiconductors is presented in [5-6]. Other relevant publications on these materials are [7-12].

One of the authors of the monograph [5], N. P. Mott, was awarded the Nobel Prize in 1978 for his important contribution to the development of the physics of non-crystalline solids. He contributed substantially to the understanding of the most crucial ideas on the nature of the electronic spectrum and on the mechanism of electric charge transport in non-crystalline semiconductors. Despite this, there are still a number of crucial experimental phenomena unexplained. The structure of amorphous substances also remains an open question. It seems that a logical way leading from clarifying structure (using demanding experimental equipment, for example) to a theory based on a known structure meets invincible obstacles already on the experimental level.

Different models are used in the creation of theoretical knowledge about amorphous materials, and the consequences of a particular model are after wards compared with experiment. In this way, suitability of a particular model is verified. It is not simple, however. No model has been suggested yet that would explain sufficiently the wide range of observed phenomena. Indeed, this may be connected to the nature of the object under discussion. Non-crystalline solids present an extremely wide variety of materials because they also include many component systems, in which the stoichiometric abundance of particular substances is not needed. Moreover, they are mostly metastable systems, and their metastable state depends on sample preparation. A little deviation in this procedure may lead to the creation of a quite different metastable state, and thus to the formation of a different non-crystalline material. A theory that would include all this complexity seems to be very demanding and complex.

1.2 Optical phenomena in non-crystalline semiconductors

The optical phenomena in non-crystalline semiconductors are of high interest. From the point of view of understanding the physical processes in non-crystalline semiconductors, it is very important to study optical properties of these materials, especially the optical absorption and luminescence (especially the photoluminescence).

In most crystalline solids, optical absorption is characterized by a sharp edge of the absorption band. Its position corresponds to the optical width of the forbidden band. However, the situation is different in the case of non-crystalline semiconductors. The absorption band near its border is smeared out and manifest itself as a tail that extends deeply into the forbidden band [5-9, 13-21]. Its profile is exponential as a rule. The exponential tails at higher temperatures tend to fit Urbach´s formula. The slope of the tails changes with the temperature decrease. At low enough temperatures, the slope of the tail rises when the temperature decreases. However, a certain parallel shift of the curves towards lower absorption efge is observed.

The nature of the absorption edge in non-crystalline (amorphous) semiconductors has been longly discussed in literature for many years. The attempts of many authors to explain the absorption edge did not gave, up to day, satisfactory results [21-23].

The exponential tails in the case of amorphous semiconductors tend to fit Urbach’s formula. At higher temperatures (above T_o), the slope of the tails, ln $\alpha(hf)$, changes with temperature in accordance with the Urbach margin (Urbach’s rule). At lower temperatures, the slope of the tails does not change with further temperature decrease. However, a certain parallel shift towards lower absorption is observed.

From among existing theories that try to explain the Urbach’s rule, none is preferred as yet. The following theories try to explain the behavior of the material:

1.2.1 The theory of bound exciton.

It is an exciton that interacts with lattice oscillations. According to Toyozawa [5,6, 24], the Gaussian shape of the exciton absorption line changes strongly if we consider the quadratic terms of mutual exciton-phonon interaction. The long-wave wing of the line changes from Gaussian to exponential. The most difficult problem to explain is why the quadratic terms exceed the linear terms.

1.2.2 The theory of broadening the absorption margin by an electric field

This is the so-called Franc-Keldysh effect [5,6,25]. Its nature is in tunneling of the Bloch states in to the forbidden band when the energy of a photon is smaller than it would be at the bottom of the allowed band. At that, the origin of strong electric fields and, especially, the explanation of temperature dependence of the tail remain questionable.

1.2.3 The theory of the exciton line broadening by an electric field.

Dow and Redfield [24] investigated the problem of absorption in a direct transition of exciton in a homogenous electric field. They pointed out that the tail shape is exponential. On this basis, they expressed a hypothesis that Urbach’s rule can be explained by broadening of the exciton absorption line by an electric field. There remains, however, a problem of explaining the origin of internal electric fields as well as the observed temperature dependence. Mott [5] assumed that just this theory could be the most acceptable one for the non-crystalline semiconductors. However, he raised some questions at the same time. Do excitons exist at all in amorphous materials? What is the origin of internal electric fields? No one has offered a satisfactory answer yet.

In amorphous semiconductors, however, there exist some specific ways to explain the origin of the exponential tails. Questions of exponential tails and of density states at the band margins were widely discussed in the scientific community [4,5]. From this point of view, the exponential tails of optical absorption should rise as a result of optical transitions between levels belonging to the tails of density states at the margins of the valence and conduction bands. It is usually assumed that these tails of density states may have an exponential shape as well. According to Mott [5], however, such an explanation is considered to be of low probability. The main argument opposing this concept is the fact that the slope of the dependence ln$\alpha(hf)$ has approximately the same slope on all semiconductors. It is doubtful to expect that the tails of density states should be equal, at least nearly, in all amorphous semiconductors.

To conclude this part, it should be stated, in accordance with Overhof [12], that as yet there is no plausible theory that would explains satisfactorily the origin of exponential tails in non-crystalline or even in crystalline semiconductors.

In this work, the results of the author’s effort to clarify physical properties of non-crystalline semiconductors in a more comprehensive way are presented. The existence of a potential barrier among individual microscopic regions of a non-crystalline solid seems to be the most typical feature of this model. It is called the barrier-cluster model. The most important optical phenomena, observed in non-crystalline semiconductors, are then explained on the basis of this model. Before all this, physical mechanisms responsible for the rise and properties of exponential tails of optical absorption are addressed. From among further important optical phenomena explained in this study, electroabsorption, photoluminescence, photoelectric conductivity, and quantum yield should be mentioned. The barrier model enables us also to explain a series of electric transport phenomena.

Up to now no satisfactory model has been proposed, in the frame of which it would be possible to explain a wider enough palette of optical and other processes in non-crystalline semiconductors. In the papers [26-33], the explanation of some optical phenomena in chalcogenide glasses on the base of a barrier- cluster model was presented.We presume that the barrier-cluster model of a non-crystalline semiconductor could be taken adequate for this aim. This model was repeatedly used for understanding some special problems of the non-crystalline solid state physics [26-33]. Naturally, one can not expect that all phenomena in non-crystalline materials can be explained by virtue of the barrier-cluster model. Nevertheless, it has allowed to describe some most typical common features for a sufficiently broad class of non-crystalline materials.

The photoluminescence based on the barrier-cluster model of a non-crystalline solid was described in some previous papers by the author [26-33]. In the current paper, luminescence processes are studied, from viewpoint of energy quantum *hf* influence upon the photoluminescence intensity (strength). Especially, we deal with an explanation of “luminescence output” incident radiation in an energy region corresponding to the exponential tail of optical absorption.

Street et al (1974) [34] discovered that the temperature dependence of the luminescence intensity in quenched a-As_2Se_3 has the form:

$$I \sim \exp(-T/T_o) \qquad (1)$$

over four orders of magnitude of the intensity, where T_o is a constant. This dependence $I(T)$ was observed for instance in [35-40].

There is a serious problem how to understand the photoluminescence and especially how to explain its temperature dependence. The luminescence is an important optical phenomenon for the theory of non-crystalline semiconductors.

The photoluminescence intensity in amorphous semiconductors decreases in time after the beginning of the illumination at low temperatures. The experiments show [5, 6, 40-42] that the originally high luminescence level decreases gradually and stabilizes at a considerably lower level after a certain time. This fatigue effect is strongest in chalcogenide glasses (Cernogora et al 1973) [43] but a comparatively weak fatiguing effect has been found recently in amorphous silicon (Morigaki et al 1980) [44]. Biegelsen and Street (1980) [45], using ESR data and Shah and DiGiovanni (1981) [46,47] using luminescence decay data concluded that fatigue in a-As_2S_3 is due to the creation of non-radiative centers by the illumination. Kirby and Davis reported the luminescence fatigue in amorphous phosphorus as early as (1980) [48]. The experimental results are presented in the papers [49-51].

Theoretical explanations of Street´s empirical law have been given by Street (1976) [52], Philips (1980) [53], Gee and Kastner (1979) [54], Highasi and Kastner (1979) [55-56].

In crystals, the temperature dependence of luminescence is usually well described by a thermally activated escape process of the trapped carrier from the luminescence center to a non-radiative center. If such a model were used for a chalcogenide glass, temperature-dependent activation energies ranging from 1 meV at low temperatures to 100 meV at high temperatures should be assumed.

Gee and Kastner (1979) and Higashi and Kastner (1979) have suggested that the Street´s formula (1) is the result of a distribution of non-radiative rates which arises, in turn, from a distribution of activation energies for the non-radiative process. It will be immediately noticed that the assumption of a single radiative rate is certainly incorrect. Indeed Highasi and Kastner (1979) showed that the time dependence (fatigue) of the photoluminescence the total light decay is determined by the very broad spectrum of radiative rates.

In present no model exists, which is able to explain sufficiently wide spectrum of physical phenomena in non-crystalline semiconductors. The existing models of luminescence in non-crystalline semiconductors were derived from the VAPs concept for these materials.

The present state of knowledge is full of many contradictions.

Recently, Tanaka has questioned the presence of the charged defects [57]. The new knowledge’s above possible cluster structure of chalcogenide glasses specially closed clusters) questioned the model based on VAPs [58-60]. In [58] we can read: “Recently, a novel model for photodarkening in a-$As_2Se(S)_3$ has been proposed. Unlike the previous ones, the new model takes into account the layered cluster structure of semiconductors.”

The problem of the structure of the non-crystalline semiconductors was studied in [61-63]. The explanation of the laws of luminescence on the base of a barrier-cluster model is presented in the papers [64-67]. This model explains the present problems with ESR experimental results. However, many questions are still open.

1.3 Structure

In spite of tremendous efforts dedicated to chalcogenide glasses, the structure of these materials is not completely understood [68-76]. Some models have been developed with the aim to explain the first sharp diffraction peak in the diffraction pattern of various non-crystalline materials.

Many years ago it was pointed out that no ESR signal was detected in amorphous chalcogenides (a-Se, a-As_2S_3). This observation, i.e. the absence of spins in chalcogenide glasses, led Anderson [68] and Street and Mott [69] to formulate their negative effective correlation energy (negative-U) models, in terms of charged defects. The model assumes the presence of dangling bonds, but with the combination of positively and negatively charged dangling bonds, D^+ and D' having respectively no and two spin-paired electrons, being energetically favored over the neutral dangling bond D^o with one unpaired electron. The defect-based version of the negative-U model was subsequently developed by Kastner, Adler and Fritzsche [70] for the case of a-Se with singly coordinated, negatively charged selenium (C_1') and a three-fold coordinated, positively charged site (C_3^+) emerged as the most likely equilibrium defect configurations. Thus, the valence alternation pair concept appeared. Up to day no direct experimental evidence was found for the valence alternation pair in chalcogenide glasses. Recently, Tanaka [57] has questioned the presence of the charged defects, on the basis of optical absorption measurements on highly purified AS_2S_3 samples.

The discoveries of the fullerenes led to the suggestion that other low-dimensional covalent systems, as e.g. chalcogenides could present special configurations similar to fullerenes or nanotubes. Fullerene-like objects and nanotubes with or without closed ends have been simulated in order to demonstrate that such special "objects" are possible at least in arsenic chalcogenides [58-60, 62, 63]. The self-organization in arsenic chalcogenides is (basically) vital for the formation of the low dimensional objects in chalcogenides**.**

Several types of closed nanoclusters of As_2S_3 were built (proposed). The fairly good agreement of several characteristics, calculated from the model, with the experimental ones, allows to conclude that a model with closed ends is very attractive.

As a consequence, the dangling bonds are naturally eliminated during the glass formation, and, therefore, no significant amount of charged coordination defects is necessary to explain the glass structure. On the contrary, the formation of high amount of VAPs is predicted during illumination, and in the light saturated state of the glass. A closed cluster model for the binary arsenic-chalcogen glasses seems to be attractive for the explanation of the structural and electronic properties of non-crystalline chalcogenides. In the same time the direct consequence of the model is the absence of the defects of coordination.

1.4 Barrier-cluster model – basic information

1.4.1 Electronic spectrum

The barrier-cluster model [26-33] assumes that there exist potential barriers in a non-crystalline semiconductor, which separate certain microregions – closed-clusters and in this way, they hinder the transport of the carriers at the margin of the conduction or valence bands. In the same time, however, the barriers have also an influence upon the optical absorption at the optical absorption edge. The influence is caused in the first line by strong electron-phonon interaction, which results in the fact that on optical transition, apart from the energy of a photon, an electron can also take the energy of a phonon. Thus, on such a transition, the total of energy taken by an electron equals the sum of the photon and phonon energies (Fig. 1). Another important factor - as far as influence of barriers is concerned - is that the absorption of light in the region of the optical absorption edge at low temperatures is usually connected with tunneling of carriers through the potential barrier. Due to this fact, the absorption process is influenced by barriers. These facts enable us to explain not only the creation of exponential tails at the optical absorption edge, but also their temperature dependence at high, as well as low, temperatures. The barrier model allows us to clarify also the luminescence and photoelectric phenomena in chalcogenide glasses. This concept gives a new look at the density of states within the forbidden band of a semiconductor and it explains why attempts to identify gap-states by various optical and other methods have failed.

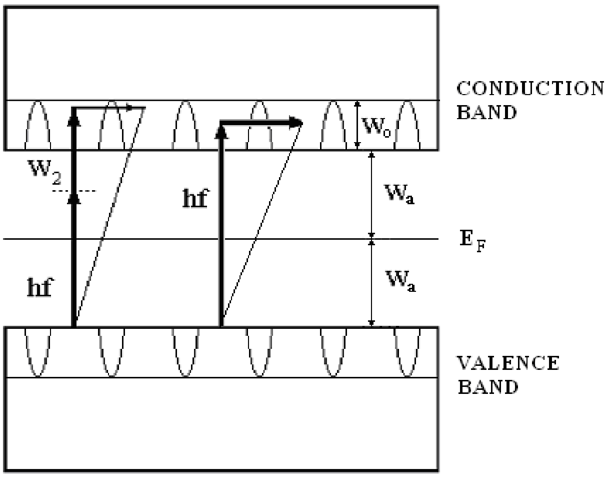

Fig. 1 *Electronic spectrum of a non-crystalline semiconductor and the optical transitions at higher* (*left*) *and at lower* (*right*) *temperature.*

The barrier-cluster model assumes that the electrons (at low energy) behave between barriers in particular regions (closed cluster) of material in a similar way as electrons in a crystal do. The potential barriers can be depicted inside the conduction and valence bands of an amorphous material, separating individual localized energy states at the edge of the band (Fig. 1). The electron levels between barriers, due to the small dimensions of the microscopic regions, exhibit a distinct discrete character. At the lower margin of the conduction band, a sub-band with carriers of low average mobility (μ_1) is created. The states with energy above the peaks of barriers are delocalised. They create a sub-band with a high average mobility (μ_2).

1.4.2 Optical phenomena and barrier-cluster model

Optical transitions in non-crystalline semiconductors at the edge of optical absorption were studied in [26-33, 64-67] from the point of view of a barrier-cluster model. It was explained why the exponential tails of optical absorption can extend deeply in the forbidden band of a non-crystalline semiconductor. It is due to strong electron-phonon interaction.

The barrier-cluster model can explain the parallel shift of exponential tails, too.

Higher temperature range: The starting point of the considerations in [26] on the base of barrier-cluster model is the assumption that due to the potential barriers in non-crystalline semiconductors proper conditions occur for a distinct absorption of light, with phonons participating in the energy exchange. An electron in an optical transition accepts not only the energy hf of a photon but also the phonon energy W_{phon}. Thus, the whole energy accepted is $hf + W_{phon}$ where W_{phon} is the energy acquired from a phonon "field". The quantity hf is positively determined by the wavelength of radiation, while $W_{phon} = W_2$ (Fig.1) has a statistical character. The average value of W_{phon} is dependent on the temperature. On the left part of the Fig. 1 is shown the optical transition at higher temperatures depicted. The transition on the right part is typical for low temperatures.

In principle, a photon can be absorbed only when the whole energy of the electron

$$hf + W_{phon}$$

is sufficient to cause a transition of the electron into the conduction band. It should be taken into account, however, that optical transitions on the energy levels lying just below the tops of the barriers will dominate at higher temperatures. In this case, the probability of transition within a single localized region is small. The levels in adjacent microregions offer more combinatory possibilities. They are connected with tunneling through barriers. Under these assumptions, the transitions on levels just below the barrier peaks will be more probable for two reasons. The transitions on lower levels will be restricted considerably by a small tunneling probability. The second reason consists in the strong electron-phonon interaction caused by the barriers. In the next we put $W_{trans} = 2W + W_o$.

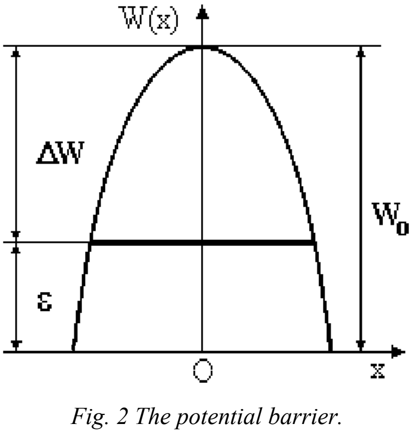

Fig. 2 The potential barrier.

The number of electrons that can acquire such deficit of energy (W_{trans} - hf) from a phonon field depends on temperature. The number of electron transitions during the irradiation of the material by "low energy" photons (and thus, also the coefficient of optical absorption α) and number of such sufficiently energetic phonons at temperature T are proportional. For the absorption coefficient it can be written [26,27] that

$$\alpha \approx \exp\left(\frac{hf - W_{trans}}{2kT}\right) \tag{2a}$$

$$\ln\alpha = \frac{hf - W_{trans}}{2kT} + const. \tag{2b}$$

or, for a particular (constant) temperature

$$\mathrm{In}\ \alpha \sim hf + \mathrm{const}$$

which is a mathematical expression of an exponential tail of optical absorption [26]. However, the slope of tails is also temperature dependent. Formulae (2a,b) are of the same kind as Urbach's formula. It explains the temperature dependence of the slope of exponential tails at higher temperature.

Low temperature range: At low temperatures, only photons with sufficient energy, exceeding $2W$ (the width of the forbidden band), can be absorbed by material (Fig. 1). The optical transition of electron is connected with a tunneling process. The "skewed" optical transition can be virtually divided into two parts [26]: The first part is a vertical transition on a virtual energy level inside its own localized region (without tunneling); the following second part represents a horizontal tunneling transition on a real level in an adjacent localized region. Thus, the mechanism of the absorption of photon in a low-temperature range is connected with the tunneling of an electron through a potential barrier. Let us remark that at lower temperatures, absorption of light in the vicinity of optical absorption edge could principally run without any tunneling process, i.e. within a single localized region. However, the probability of such transitions is small due to a distinctly discrete character of the lowest levels as well as due to a small number of such levels in a single micro-region. Therefore, absorption connected with tunneling to adjacent regions is more probable.

1.4.3 Some remarks on the parallel shift of the exponential tails of the optical absorption at low temperatures

In this section we discuss the parallel shift of the exponential tails of optical absorption in non-crystalline semiconductors at low temperatures.

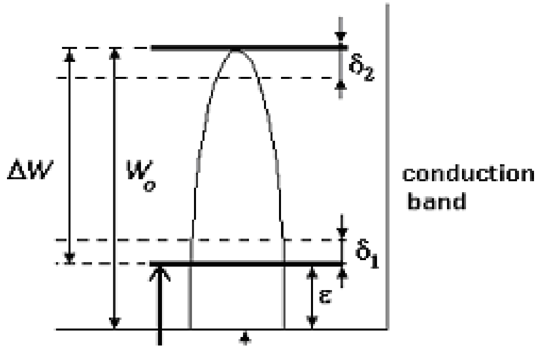

Fig. 3. The influence of temperature on the process of tunneling of electron trough the potential barrier.

The absorption of light at low temperatures and photon energy, hf, from the interval $2W < hf < 2W + W_o$ is, according to the barrier-cluster model connected with the tunneling of the electrons through the potential barrier (Fig. 1,2). Probability, p, of the tunneling depends on the energy level, on which the tunneling runs. In the case of a parabolic potential barrier (Fig. 2), the dependence of potential energy $W(x)$ of electron on its position can be denoted as

$$W(x) = -ax^2 + W_o$$

W_o, means the height of the barrier from the bottom of the conduction band and the quantity a describes the width of the barrier. For the probability of the tunneling it can be written [26]

$$p \approx \exp\{-A\,\Delta W\} \qquad (3)$$

where A is a constant depending on dimensions of the barrier

$$A = \left\{-\frac{\pi}{\hbar}\sqrt{\frac{2m}{a}}\right\}$$

and ΔW is the energy difference between the energy level of peaks of potential barriers and the energy level on which the tunneling is running, m – mass of the electron.

Should an electron take only the photon energy on absorption, we could write on the base of Fig. 2, 3

$$\Delta W = 2W + W_o - hf \qquad (4)$$

The probability of the tunneling is determined first of all by the energy of the absorbed photon. Phonons play a role in the low-temperature absorption.

1.4.4 The influence of temperature on the optical absorption

In papers [26, 28], the effect of temperature on electron tunneling across barriers was studied (Fig. 2,3). It was shown there, that for the quantity ΔW the relation (4) had to be replaced by the relation

$$\Delta W = 2W + W_o - hf - CT \qquad (5)$$

so that the relation (3) should take the form

$$p \approx \exp\left[-A\left(2W + W_o - (hf + CT)\right)\right] \qquad (6)$$

It was assumed, that $\Delta W(T) = \Delta W(0) - \delta_1 - \delta_2$ (Fig. 3) and that the values δ_1, δ_2 were linearly dependent on the temperature.

The coefficient of optical absorption of light, α, is directly proportional to probability, p (rel. 6), so that

$$\alpha \approx p \qquad (7)$$

Based on (3,6,7), the absorption coefficient would be

$$\alpha \approx p \approx \exp\left[-A\left(2W + W_o - (hf + CT)\right)\right] \qquad (8)$$

Or

$$\alpha \approx \exp[A(hf + CT)] \qquad (9)$$

This relation gives a true picture not only for experimentally observed exponential tails of optical absorption at low temperatures, which were already clarified in [26], but also for the parallel shifting of these towards lower absorption, with decreasing temperature.

As far as the dependence $\alpha(hf)$ is concerned, it also follows from (9) that

$$\alpha \approx \exp(Ahf) \qquad (10)$$

In this article we present a new view on the photoluminescence - we attempt to explain the temperature dependence of photoluminescence and its fatigue, i.e. its stabilization in the course of time.

We submit the explanation of Street's formula (1) representing the temperature dependence of photoluminescence and experimental observations concerning luminescence.

1.5 Optical absorption at low temperatures

At low temperatures, the absorption of photons is possible only if the photon energy hf is higher than the width $2W_a$ of the forbidden band. An electron, which absorbs a photon at the zero thermodynamic temperature, acquires the energy hf. At non zero temperatures, phonons can also supply a certain small quantum of energy to the electron which has absorbed a photon. This supplied quantum of energy depends on the temperature and is statistically determined. Thus, the electron absorbs the energy $hf + \delta_1(T)$, where $\delta_1(T)$ is the average energy supplied by phonons at the temperature T. The quantity $\delta_1(T)$ is assumed to be proportional to the thermodynamic temperature. Thus $\delta_1(T) = K_1T$, where K_1 is a positive constant. This proportionality is in agreement with the fact, that the average energy of absorbed phonons is proportional to k_BT, where k_B is the Boltzmann constant. Hence, the energy tunnelling level is higher than it is at the zero thermodynamic temperature (Fig. 5). At the higher energy level, the probability of the tunnelling is higher. It causes the increase in the absorption.

The optical absorption is also influenced by the temperature dependence of the forbidden band of non-crystalline semiconductors. It is known from experiments that the width of forbidden band decreases with the increase in the temperature. Hence, the quantity $2W_a$ also decreases with the increase in the temperature T. From this follows, that the height of the peak of potential barrier, measured relative to the top of the valence band, is also reduced by some amount δ_2 (Fig. 5). The quantity δ_2 is also assumed to be proportional to the thermodynamic temperature. Thus, $\delta_2 = \delta_2(T) = K_2T$, where K_2 is a positive constant. This assumption is in agreement with the results of experiments in a large range of temperatures. Thus, one can write

$$\Delta W(T) = 2W_a + W_o - hf - \delta_1(T) - \delta_2(T), \quad (9)$$

$$\Delta W(T) = 2W_a + W_o - hf - CT , \quad (10)$$

where $C = K_1 + K_2$.

Then, it follows from (4) and (10) that

$$\ln\alpha = A(hf + CT) + const. \quad (11)$$

The expression (11) is the generalization of the relation

$$\ln\alpha = A(hf) + const.$$

used for instance in [28-30]. When the temperature drops from T_1 on T_2, then lnα changes by the amount

$$\Delta\ln\alpha = AC(T_2 - T_1). \quad (12)$$

The relation (12) expresses the parallel shift of exponential tails caused by temperature changes. It is in agreement with experimental data [1-7].

From (11) it follows that,

$$C = \frac{1}{A}\frac{d(\ln\alpha)}{dT}. \quad (13)$$

We notice that the constant C according to [31] is equal to the negative value of the thermal coefficient of the optical forbidden band gap width of a chalkogenide glass. An optical gap width decreases linear with increasing temperature in a broad temperature interval – as it is shown in [44] – consequently the coefficient C more or less is constant. This is conformable with submitted model.

1.6 Photoluminescence in chalcogenide glasses

A possible concept of the physical nature of photoluminescence in chalcogenide glasses at low temperatures, from the point of view of the barrier-cluster model, is presented in Fig. 1 [26-33]. An electron during the optical transition, linked with tunneling, arrives at an adjacent or a neigbouring region with an energy level below the peak level of potential barriers. Electron is free only within its own localization region. Its wave function would be localized practically in its own micro-region between the neigbouring barriers.

1.6.1 Bound electron-hole (e-h) couples

Due to the Coulomb interaction, a bound state of an *e-h* couple arises. As a consequence, a new energy level is formed in the forbidden band. Let us assign this level formally to that localization region where the electron finds itself. This level is below the bottom of the conduction band. Levels of this kind will occur not only in the neighboring micro-region (cluster), but also in the more distant regions. The position of these levels depends on the distance from the "mother" micro-region (for the sake of simplification, we suppose that the hole did not move). With increasing distance, these levels will approach the bottom of the conduction band.

In Fig. 4, some of these levels are depicted on both sides of the hole (in a one-dimensional model). These levels create a kind of a "funnel" of levels. A new energy level will appear not only in adjacent micro-regions but also in the original mother micro-region with the hole. The electron level in the mother region is the lowest one among all levels of the funnel.

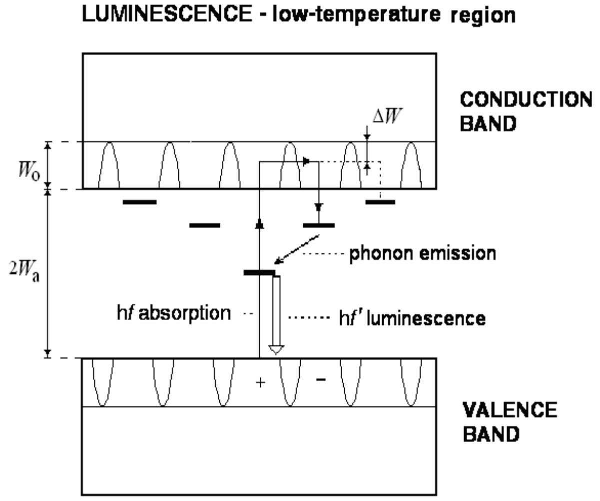

Fig. 4. The processes connected with photo-luminescence

However, discrete levels of excited states in a given region also belong to each level of the funnel, as the lowest energy level of the given localization region. These levels are not shown in the diagram

1.6.2 Approaching processes

At low temperatures, an optically excited electron will, with a high probability, gradually come back to the mother region of the hole. Such an approach is connected with tunneling and diffusion. The approaching jumps "region-by-region", are due to an interaction with phonons. Without phonons, such an approaching process would not be possible. These approaching processes are in principle not radiative. An electron loses gradually a considerable part of its energy. In the last phase, a non-radiative transition occurs in its own a localization region. In this region, the radiative optical recombination of the *e-h* pair occurs, accompanied by emission of a luminescence photon, whose energy is considerably lower than that of photons of the exciting radiation. A distinct Stokes shift will occur.

If no other disturbing processes take place, a stationary state with a relatively high level of luminescence would take place quickly within the material. In fact, this corresponds rather well to a realistic situation in the first phase of irradiation. However, the state of the high luminescence weakens rather quickly.

1.6.3 The influence of free electrons on photoluminescence

When irradiating a non-crystalline semiconductor by a flux of photons at low temperatures under conditions described above, free electrons are practically formed only by a multiple-tunneling of a small amount of electrons, which perform the optical transition. The slow rise of concentration of free electrons is caused by the relatively low probability of the multiple-tunneling process. The concentration of the free electrons in semiconductor stabilizes only after a long time, when some dynamical equilibrium of two mutually opposing effects establishes, i.e. the process of producing free electrons and the process of their annihilation by joining holes so that new bound *e-h* pairs are created.

When explaining the laws of photoluminescence on the basis of the barrier-cluster model, an extremely significant assumption is accepted in our considerations, namely that free electrons, by their effect, stimulate the non-radiant recombination of bound *e-h* pairs (as a kind of a catalyst), and thus, they reduce the number of radiant transitions. So, ultimately, free electrons markedly influence the luminescence process. The free electron remains free after such individual catalyst process and continues triggering non-optical transitions, acting as a catalyst.

1.6.4 Mechanism of free electrons origin

It was already said that a source of free electrons in a non-crystalline matter during photo-irradiation at low temperatures is a manifold tunneling of a small electron fraction at the process of the optical absorption connected with tunneling (Fig. 4). For this mechanism, it is essential that the majority of electrons execute a tunneling through one potential barrier at the optical transition. Some electrons drive a tunnel s - times across s barriers consecutively at the optical transition. In this manner, electrons overcome a long distance from their original region (together with a corresponding hole) and become free. An electron will no longer be bounded with a hole by the Coulomb force. In our model it is assumed that free electrons then activate non-radiating transitions of bounded pairs *e-h*. These will not contribute to the luminescence.

According to [26-33], the probability, *p*, of a single tunneling of such a particle is proportional to the expression

$$p \sim \exp\left(-A\left(\Delta W - CT\right)\right) \qquad (14)$$

For the probability p^s of the multiple-tunneling of the electron through *s* barriers, we can write

$$p^s \sim \exp(-\mathrm{As}.(\Delta W - CT) \qquad (15)$$

The probability of the creation of a free electron is proportional to expression (15). Since the probability is small, the number of free electrons will slowly increase after the beginning of the illumination of the glass. Therefore, the increase rate of non-radiant recombination of bound *e-h* couples will be slow. This is why the process of the stabilization of luminescence will be slow.

In Ref. [26-33], the empirical Street's law has been derived under these assumptions

$$I \approx \exp\left(-\frac{T}{T_0}\right) \qquad (16)$$

This expresses the dependence of the photo-luminescence on the temperature in a low temperature range.

2. Dependence of photoluminescence on the absorbed energy quanta

2.1 Experimental observations

Now we are going to treat the relationship between an optical absorption and a photoluminescence radiation.

Experimental research on the photo-luminescence in an energy region of photons belonging to the exponential tail of an optical absorption showed that at the lower photon energy, the photoluminescence intensity increases with the increase of the photon energy, analogously to the absorption. The photoluminescence copies the course of the absorption in this region. One can speak of a correlation in this case. This fact can be understood if we assume that in this region of photon energies nearly all *e-h* pairs generated by light recombine radiatively. At higher energies of the activating photons in a region of an exponential tail of the absorption will still increase exponential with increasing photon energies but the luminescence after reaching its maximum begins to decrease at increasing energy of the photons.

This is to be understood as follows: by an energy increase of the activating photons the number of e-h pairs undergoing a non-radiative recombination increases gradually. This is probably due to the effect of free electrons which stimulate the non-radiative recombination.

2.2 Basic data from viewpoint of the barrier-cluster model

At low photon energies and low temperatures, a number of free electrons in the material are negligible small. The radiative recombination almost does not take place in this case. Nearly all recombined transitions are radiative. More bounded *e-h* pairs arise from absorption in the substance and the large number of phonons will be emitted in the luminescence process. The luminescence will copy the absorption.

At higher photon energies a tunneling of electrons through barriers will be in progress at higher energy levels. This increases the probability of single tunneling. The probability of the s-multiple tunneling of electrons overriding long distances will rise much faster. Thereby, with the energy increase of activating photons a free electron production will increase in the substance essentially and thus also the number of the non-radiate recombination *e-h* pair. The radiative transition number as well as the luminescence “niveau”, will no longer be proportional to the number, of absorbed photons corresponding to the number of generated *e-h* pairs. With increasing the photon energy, the luminescence increase first slows down, and then stops and finally the luminescence begins die away. In the light of the above mentioned ideas, one can understand the experimentally observed dependencies.

2.3 Mathematical description of development of a luminescence process

As was already said, the probability of a free electron appearance at the mechanism of multiple tunneling during absorption at the temperature T and energy of activating photon hf is given as follows

$$P^s \sim \exp(\mathrm{As}.(hf+CT)) \tag{17}$$

The level of luminescence of a non-crystalline semiconductor will depend on the concentration, N, of the bound pairs *e-h*. This value depends on the concentration, n, of the free electrons in the material. The time dependence of the concentrations n and N can be described by the system of two differential equations:

$$\frac{dN}{dt} = C_1 - C_2N - C_3C_1\exp\,(sA.(hf+CT) - \\ - C_4Nn + C_5n^2 \tag{18}$$

$$\frac{dn}{dt} = C_3C_1\exp\,(sA.(hf+CT)) - C_5n^2 \tag{19}$$

Here dN/dt is the change of the concentration of the bound *e-h* pairs per unit time, dn/dt is the change of the concentration of the free electrons per unit time. The first term, C_1, at the right hand side of the equation (18) represents the number of pairs produced by incident photons per unit time. The term C_2N means the number of radiative recombinations of bound *e-h* couples per unit time. The term $C_3C_1.\exp\,(sA\,(hf+CT))$ is, according to (17), the number of multi-tunneling electrons through *s*-barriers, and simultaneously the number of newly created free electrons. The term C_4Nn means the number a non-radiant recombination of bound pairs having passed through a non-radiant transition under the catalyst influence of free electrons. The term C_5n^2 is the number of free electrons captured by a free hole and creating a new bound *e-h* couple with it.

2.4 Steady (stabilized) luminescence

After a sufficiently long exposition of a non-crystalline semiconductor, a real stationary state establishes when

$$\frac{dN}{dt} = 0,\ \frac{dn}{dt} = 0 \tag{20a,b}$$

For this state, we obtain from (18,19)

$$0 = C_1 - C_2N - C_3C_1\exp\,(sA(hf+CT)) - C_4Nn + C_5n^2 \tag{21}$$

$$0 = C_3C_1\exp\,(sA.(hf+CT)) - C_5n^2 \tag{22}$$

The first equation will simplify with respect to validity of the second one. Hence, the system acquires the form

$$0 = C_1 - C_2N - C_4Nn \tag{23}$$

$$0 = C_3C_1\exp\,(sA.(hf+CT)) - C_5n^2 \tag{24}$$

From equation (15) it follows for a stationary value $N = N_2$ that

$$N_2 = \frac{C_1}{C_2 + C_4n} \tag{25}$$

where n is the stationary value of concentration of free electrons. Since

$$N_2 = \frac{C_1}{C_2 + C_4n} \le \frac{C_1}{C_2} = N_1 \tag{26}$$

The value N_2 is lower than the value N_1 determined by equation (25) if $n = 0$. Thus, with increasing the number of free electrons, the concentration of bound pairs decreases from the value N_1 (immediately after the start of illumination) to the value N_2. This decrease can be multiple – and this corresponds to experimental results. In a particular case, if concentration, n, of free electrons reaches a certain value, the condition

$$C_2 << C_4n \tag{27}$$

can be satisfied. Then, equation (17) acquires the approximate form

$$\mathrm{N}_2 = \frac{C_1}{C_4n} \tag{28}$$

2.5 Generalized Street’s law of luminescence

If we express concentration n from (24) and insert it in (28), we obtain for $N = N_2$

$$N_2 = const\,.\,\exp\,(-\tfrac{1}{2}\,sA(hf+CT)) \tag{29}$$

Where

$$const = \left[\frac{1}{C_4}\sqrt{\frac{C_1C_5}{C_3}}\right] \tag{30}$$

We can write for stabilized luminescence $I = I_2 \sim N_2$ and thus

$$I \sim \exp\left(-\frac{hf}{H_0}\right)\exp\left(-\frac{T}{T_o}\right) \qquad (31)$$

where

$$T_o = \frac{2}{\mathrm{sAC}} \qquad (32)$$

$$H_o = \frac{2}{\mathrm{sA}} = CT_0 \qquad (33)$$

If the temperature is constant then it holds

$$I \sim \exp\left(-\frac{hf}{H_O}\right) \qquad (34)$$

At the constant energy *hf*, Street's law of luminescence (15) follows from (31).

The relation (23) represents a generalization of the empirical Street's law. This generalized Street's law gives quantitative dependency of luminescence on the temperature, as well as on the photon energy of the activating rays. It is available in a range of low temperatures and energies *hf* in the upper part of an exponential tail (under the condition $nC_4 >> C_2$).

2.6 Comparison with experiment

From relation (32-34), it follows that at a constant temperature, the photoluminescence wich increasing photon energy begins to decrease. The slope of the straight line

$$\ln I\,(hf) = -\frac{hf}{CT_0} \qquad (35)$$

is - $1/CT_0$. The approximate value of this slope for the glass As_2S_3 can be obtained when using relations (33..25) and (32..24) inserting for T_o = 27 K and $C = 7.10^{-4}$ eVK^{-1}. Then $1/CT_0 \sim 35$ $(eV)^{-1}$.

If one analyses the plot of the luminescence dependence on the photon energy for the glass As_2S_3 obtained from experiment and published in Ref. [5,6] and determines the slope of the graph at the place of the maximum decrease of the function ln(*I*), one obtains the value comparable with that we have introduced above.

3. Discussion

3.1. New arguments confirming suitability (correctness) of the model

In the next part we present several facts in support of the concept of the role of free electrons, which were not published so far.

Suppose that there are conditions in a non-crystalline solid when free electrons practically do not emerge via optical process (i. e. through the above described mechanism of *s*-fold tunnelling). It would happen, for example, if tunnelling through barriers ran on low energy levels. In such a case the probability of *s*-fold tunnelling would be minor. Free electrons of optical origin would have partically zero concentration. However, it does not mean that free electrons of other origin, e. g. electrons produced via temperature mechanism cannot exist in such a solid.

In case the electrons are of thermal origin, then for their concentration is valid the relation

$$n \approx \exp\left(-\frac{W}{kT}\right) \qquad (36)$$

In a special case, if $nC_4 > C_2$, it follows from (17) and (36) for the luminescence intensity

$$I \approx \exp\left(\frac{W}{kT}\right) \qquad (37)$$

However, this is quite different relationship than that, which is represented by the Street´s luminescence law. The dependence (37) expressed in the form

$$\ln I\left(\frac{1}{T}\right) \qquad (38)$$

represents a straight line with a positive directive. Thus, photoluminescence rapidly decreases with increasing temperature owing to the growth of concentration *n* of free thermal electrons. The concentration of optically excited free electrons (via mechanism of *s*-fold tunnelling) is unimportant in this case.

3.2 Confrontation of two dependencies

It is possible in this way also to explain e. g. the experimentally observed temperature dependence of photoluminescence for amorphous silicon *Si* as described in [6].

Let us stop for a while over the presented picture in [6]. Apart from a straight line dependence of photoluminescence on the argument (1/*T*), also a graph is depicted that displays the dependence of concentration of photoelectrons (photoconductivity) on the argument (1/*T*). It might seem at first sight that these two dependences contradict our described concept about the role of free electrons. It can be clearly seen from the graph that photoluminescence rapidly decreases with increasing temperature right in the place where the concentration of free electrons *n* is constant, i. e. stable. It is in direct contrast with our concept of the role of free electrons. We will demonstrate however, that this is only a seeming discrepancy. But a clarification of this dilemma needs a little more detailed consideration of photoconductivity.

It is well known from the photoconductivity in non-crystalline semiconductors that in the low temperature region it increases with increasing temperature. With further increase in temperature it reaches a maximum and then it falls down. Obviously, the same will apply to the concentration of photoelectrons in dependence on temperature, but in connection with the depicted graph - its last phase (i. e. decrease of photoconductivity with increasing the temperature in the high temperature region) is missing.

Let us observe here that in the high temperature region the photoconductivity curve begins to decrease because the mechanism of recombination is changing. This change is a consequence of thermal carriers, that begin to dominate over the photo carriers. Therefore, it is no surprising that photoconductivity electrons will not run any longer, but the predominating thermal electrons. So, suppression of photoluminescence with increasing temperature in the picture does not relate to the stabilized concentration of photoconductivity electrons, but to a rapid growth of concentration of free thermal electrons. Thus, these two graphs do not represent any dilemma as far as the role of free electrons in a photoluminescence process is concerned.

3.3. Influence of a strong electric field on photoluminescence

Strong electric field E – as it is known from experimental observations – depresses the level of the photoluminescence I in non-crystalline semiconductors. From the barrier-cluster model viewpoint this effect is acompanied with influence of the electric field which increases the number of free electrons. These electrons, during process of the optical absorption become free due to the multiple tunneling across the barriers. The increased number of free electrons (stimulating the non-radiative recombination) implices a lowering of the radiative recombination number and simultaneously the lowering of the level of luminescence.

Effect of the field on a process of the multiple tunneling lies in the strong electric field affects the electron energy during of the tunneling through the potential barriers. The energy of a moving electron in the direction of the acting electric force increases, in the opposite direction decreases. Theoretical analyses gives the result [77]

$$I(E) = I(0)\sqrt{\frac{1}{1+0.5\,B_3^{\,2}E^2}} \qquad (39)$$

or approximately

$$I(E) = I(0)\left(1-0.25\,B_3^{\,2}E^2\right) \qquad (40)$$

where B_3 is constant. The intensity of the photo-luminescence decreases quadratic with the electric field intensity E. The relations (39) and (40) are but more general.

3.4 Optical production of phonons

Chalcogenide amorphous semiconductors are distinguished by a strong electron-phonon interaction. On absorption of light, a photo-production of phonons may also occur. They can influence the absorption process. Initially, low optical absorption can increase due to photons produced by light itself, even at a low temperature. This process must play an important role in the measurement of absorption at very low temperatures. At low temperatures, the concentration of light-produced phonons can prevail over the concentration of phonons with a thermal origin. This phenomenon may apply in some crystalline chalcogenides, too.

Note: Let us remark that the barrier-cluster model of the non-crystalline semiconductors in the actual state of its development (as barrier model) was used for the explanations of electric transport phenomena in weak and high electrical fields and at high pressure [78-83]. The idea was presented by the author’s works as early as in 1972-1983. At that time nothing was known about fullerene or nanotube cluster types. Designation of the barrier-cluster model was used by author for the first in 2006.

Note: A further literature about the optical phenomena in chalcogenide glasess can be found in [84 - 105].

4. Conclusions

It is shown in this article, that several experimental data relevant for luminescence activated by irradiation in a region of the exponential tail can be explained in the frame of the barrier-cluster model. Additional assumption to the model is: free electrons stimulate non-radiative recombination of bounded electron-hole pairs. When the energy of activating photons increases, the probability of the multiple tunneling also increases which implies an increase of an optical production of free electrons. This leads to the damping of photoluminescence. Then, in a certain range of an exponential tail comes into operation that by an increase of absorption at increasing energy hf the luminescence after reaching maximum begins to sink.

To support the role of free electrons as an accelerant of non-radiative transitions in a non-crystalline substance, several arguments can be introduced. One of them is that our model enables the derivation of the well-known Street’s formula for the luminescence radiation. Furthermore, it makes possible to give reason for successive decrease of the luminescence intensity with time, beginning at the moment when activating radiation comes into operation.

Study of the optical properties of chalcogenide glasses is very important for the determination of the electronic band structure as well as other optical parameters, such as optical energy gap and refractive index.

Acknowledgement

At the end, I want to thank Prof. Viktor Bezak from the Faculty of Mathematics, Physics and Informatics, Commenius University in Bratislava and Prof. Frantisek Culık from the FCE, Slovak University of Technology in Bratislava for valuable discussions on this topic.

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